Supplementary Information

Ligand-free in situ generated cobalt nanoparticles catalyst for (Z)-selective transfer semihydrogenation of alkynes

Shunbin Yang,[a] Dengju Zhang,[a] Weiguo Zuo,[b] Guanqun Wang,[a] Chengtao Wang,[a] Jiyang Guo,[b] Duona Fan,[a] Song You*[b] and Xian Jia*[a]

[a] *School of Pharmaceutical Engineering, Shenyang Pharmaceutical University, Shenyang, China.*

[b] *School of Life Sciences and Biopharmaceutical Sciences, Shenyang Pharmaceutical University, Shenyang, China.*

E-mail: jiaxian206@163.com.

† These authors contributed equally to this work.

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General Information

All chemicals were purchased from Leyan (Shanghai, China), Energy chemical (Anhui, China).

^{1}H NMR spectra were recorded using 600 and 400 MHZ spectrometer. Transmission electron microscopy (TEM) images were obtained using TESCAN MIRA LMS Oxford Xplore 30. Malvern laser particle size analyzer (MS) images were obtained using Nano-ZS ZEN3700. Reaction mixtures were analyzed by SCION 456-GC (SCION Instruments) system by using Rtx-5 capillary column (0.32 mm × 30 m, 0.25 μm film thickness: Restek).

General procedure for the preparation of alkynes 1b-1n [1]

The corresponding aryl iodide (1.2 equiv.), $PdCl_2(PPh_3)_2$ (1-2 mol%), CuI (1-2 mol%), PPh_3 (1-2 mol%) and aryl acetylene (3 mmol) were added to a 50 mL round bottom flask with a stir bar under an atmosphere of nitrogen. Then tetrahydrofuran (5 mL) and triethylamine (5 mL) were added sequentially. The reaction mixture was then stirred at room temperature overnight. Afterwards 10 mL of water was added and the reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic fractions were washed with brine and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as the eluent.

Typical procedure of the CoNPs-catalyzed semihydrogenation of alkynes 1a-1l and 1r

To a 2 mL heavy-wall screw-capped flask, alkyne substrate (0.25 mmol), $CoCl_2 \cdot 6H_2O$ (10 mg, 0.04 mmol), ammonia-borane ($NH_3 \cdot BH_3$) (12 mg, 0.375 mmol) and methanol (1 mL) were added. Then the mixture was stirred at 70 °C for 3 h followed by cooling to room temperature. The reaction was monitored by TLC. When the reaction was complete, the resulting solution was concentrated in vacuum. The crude products were purified by chromatography on silica gel to give *cis*-alkene product.

Typical procedure of the CoNPs-catalyzed semihydrogenation of alkynes 1m and 1n

To a 2 mL heavy-wall screw-capped flask, alkyne substrates (0.25 mmol), $CoCl_2 \cdot 6H_2O$ (8 mg, 0.034 mmol), $NH_3 \cdot BH_3$ (8 mg, 0.25 mmol) and methanol (1 mL) were added. Then the mixture was stirred at 60 °C for 1 h followed by cooling to room temperature. The reaction was monitored by TLC. When the reaction was complete, the resulting solution was concentrated in vacuum. The crude products were purified by chromatography on silica gel to give *cis*-alkene product.

The procedure for transfer hydrogenation of terminal alkynes 1o-1q

To a 2 mL heavy-wall screw-capped vial, $CoCl_2 \cdot 6H_2O$ (15 mg, 0.063 mmol), $NH_3 \cdot BH_3$ (6 mg, 0.2 mmol) and methanol (1 mL) were added. Then the mixture was placed at 70 °C for 20 min followed by cooling to room temperature. alkyne substrates (**1o-1q**) (0.25 mmol)，$NH_3 \cdot BH_3$ (12 mg, 0.375mmol) were added, the mixture was placed at 70 °C for 2.5 h followed by cooling to room temperature. The reaction was monitored by TLC. When the reaction was complete, the resulting solution was concentrated in vacuum. The crude products were purified by chromatography on silica gel to give product **2o-2q**.

The procedure of gram-scale synthesis of (*Z*)-stilbene

To a 30 mL heavy-wall screw-capped vial, diphenylacetylene (**1a**) (1g, 5.6 mmol), $CoCl_2 \cdot 6H_2O$ (214 mg, 0.90 mmol), $NH_3 \cdot BH_3$ (260 mg, 8.4 mmol) and methanol (20 mL) were added. Then the mixture was stirred at 70 °C for 3 h followed by cooling to room temperature. The yield of (*Z*)-stilbene was determined by GC.

The procedure of recyclability experiment

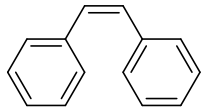
To a 2 mL heavy-wall screw-capped vial, **1a** (44 mg, 0.25 mmol), $CoCl_2 \cdot 6H_2O$ (10 mg, 0.04 mmol), $NH_3 \cdot BH_3$ (12 mg, 0.375 mmol) and methanol (1 mL) were added. Then the mixture was placed at 70 °C for 3 h followed by cooling to room temperature (no use magnetic stirrer: CoNPs can be adsorbed by magnetic stirrer, which makes it difficult to separate CoNPs from the reaction mixture and reduce the contact area between CoNPs and **1a** before the second recyclability experiment. So the reaction vial should be shaken once every twenty minutes). When the reaction was complete, the reaction mixture was removed and CoNPs was retained in vial by magnet. Then methanol was added to wash CoNPs for three times. Finally, **1a** (0.25 mmol), $NH_3 \cdot BH_3$ (0.375 mmol) and methanol (1 mL) were added for the second procedure of semihydrogenation of **1a** (1-2 mg $CoCl_2 \cdot 6H_2O$ was added before each recyclability experiment to avoid the impact of loss of CoNPs).

The procedure of gram-scale synthesis of Combretastatin A-4

To a 30 mL heavy-wall screw-capped vial, Phenol, 2-methoxy-5-[2-(3,4,5-trimethoxyphenyl) ethynyl] (1g, 3.2 mmol), $CoCl_2 \cdot 6H_2O$ (122 mg, 0.51 mmol), $NH_3 \cdot BH_3$ (148 mg, 4.8 mmol) and methanol (20 mL) were added. Then the mixture was stirred at 70 °C for 3 h followed by cooling to room temperature. The crude products were purified by chromatography on silica gel to give Combretastatin A-4.

NMR spectra data of products

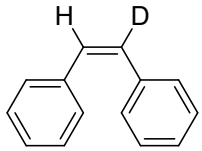
(*Z*)-1,2-diphenylethene



(*Z*)-2a

Colourless liquid. Yield 96%. known compound [1].

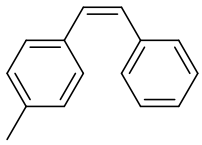
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.16 (m, 10H), 6.60 (s, 2H).



Colourless liquid. Yield 96%. known compound [1].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 – 7.10 (m, 10H), 6.53 (s, 1H).

(*Z*)-1-methyl-4-styrylbenzene

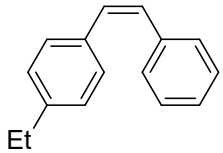


(*Z*)-2b

Colourless oil. Yield 90%. known compound [1].

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.28 – 7.19 (m, 5H), 7.12 – 7.09 (m, 2H), 7.06 (d, J = 7.8 Hz, 2H), 6.58 (s, 2H), 2.26 (s, 3H).

(*Z*)-1-ethyl-4-styrylbenzene

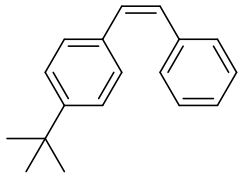


(*Z*)-2c

Colourless liquid. Yield 87%. known compound [2].

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.28 – 7.20 (m, 5H), 7.15 – 7.12 (m, 2H), 7.09 (d, J = 8.1 Hz, 2H), 6.59 (s, 2H), 2.56 (q, J = 7.6 Hz, 2H), 1.15 (t, J = 7.6 Hz, 3H).

(*Z*)-1-(tert-butyl)-4-styrylbenzene

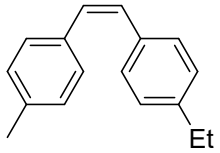


(*Z*)-2d

Colourless liquid. Yield 91%. known compound [2].

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.30 – 7.22 (m, 7H), 7.17 – 7.13 (m, 2H), 6.61 – 6.55 (m, 2H), 1.24 (s, 9H).

(*Z*)-1-ethyl-4-(4-methylstyryl) benzene

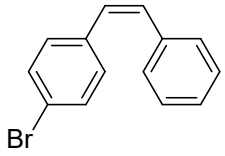


(*Z*)-2e

Colourless liquid. Yield 92%. known compound [3].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 – 7.08 (m, 4H), 6.98 (dd, *J* = 12.1, 7.9 Hz, 4H), 6.44 (s, 2H), 2.54 (q, *J* = 7.6 Hz, 2H), 2.24 (s, 3H), 1.15 (t, *J* = 7.6 Hz, 3H).

(*Z*)-1-bromo-4-styrylbenzene

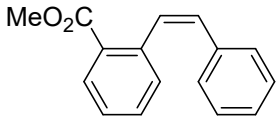


(*Z*)-2f

Colourless liquid. Yield 90%. known compound [2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.26 – 7.19 (m, 5H), 7.11 – 7.09 (m, 2H), 6.63 (d, *J* = 12.1 Hz, 1H), 6.50 (d, *J* = 12.2 Hz, 1H).

methyl (*Z*)-2-styrylbenzoate

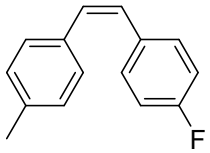


(*Z*)-2g

Colorless liquid. Yield 72%. known compound [4].

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.94 – 7.90 (m, 1H), 7.43 – 7.38 (m, 2H), 7.19 – 7.14 (m, 4H), 7.04 – 7.00 (m, 2H), 6.98 (d, *J* = 12.2 Hz, 1H), 6.65 (d, *J* = 12.2 Hz, 1H), 3.81 (s, 3H).

(*Z*)-1-fluoro-4-(4-methylstyryl) benzene

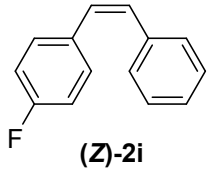


(*Z*)-2h

Colorless liquid. Yield 92%. known compound [5].

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.28 – 7.23 (m, 2H), 7.12 – 7.06 (m, 6H), 6.61 – 6.54 (m, 2H), 2.26 (s, 3H).

(*Z*)-1-fluoro-4-styrylbenzene

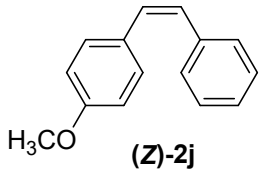


(*Z*)-2i

Colorless oil. Yield 93%. known compound [1].

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.32 – 7.15 (m, 7H), 7.12 – 7.05 (m, 2H), 6.64 (d, J = 6.3 Hz, 1H), 6.61 (d, J = 6.3 Hz, 1H).

(*Z*)-1-methoxy-4-styrylbenzene

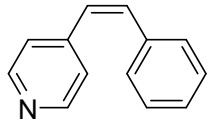


(*Z*)-2j

Yellow liquid. Yield 88%. known compound [1].

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.30 – 7.18 (m, 5H), 7.17 – 7.13 (m, 2H), 6.84 – 6.78 (m, 2H), 6.57 – 6.50 (m, 2H), 3.72 (s, 3H).

(*Z*)-4-styrylpyridine

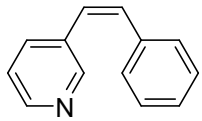


(*Z*)-2k

Yellow liquid. Yield 75%. known compound [1].

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.46 – 8.44 (m, 2H), 7.32 – 7.25 (m, 3H), 7.23 – 7.20 (m, 2H), 7.16 – 7.14 (m, 2H), 6.87 (d, J = 12.2 Hz, 1H), 6.62 (d, J = 12.2 Hz, 1H).

(*Z*)-3-styrylpyridine

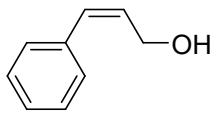


(*Z*)-2l

Yellow oil. Yield 82%. known compound [3].

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.46 (d, J = 39.2 Hz, 2H), 7.52 (dt, J = 8.0, 2.0 Hz, 1H), 7.27 – 7.18 (m, 5H), 7.14 (dd, J = 8.0, 4.8 Hz, 1H), 6.76 (d, J = 12.2 Hz, 1H), 6.55 (d, J = 12.2 Hz, 1H).

(*Z*)-3-phenylprop-2en-1-ol

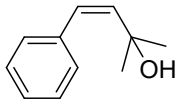


(*Z*)-2m

Orange liquid. Yield 87%. known compound [1]

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.44 – 7.27 (m, 5H), 6.51 (dt, J = 12.0, 2.0 Hz, 1H), 5.86 (dt, J = 12.0, 6.1 Hz, 1H), 4.95 (d, J = 5.4 Hz, 1H), 4.29 (dd, J = 5.1, 2.6 Hz, 2H).

(*Z*)-2-methyl-4-phenylbut-3-en-2-ol

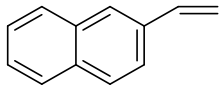


(*Z*)-2n

Colorless liquid. Yield 78%. known compound [1].

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.47 (dd, J = 7.9, 1.4 Hz, 2H), 7.29 (dd, J = 8.4, 6.8 Hz, 2H), 7.22 – 7.17 (m, 1H), 6.30 (d, J = 13.0 Hz, 1H), 5.71 (d, J = 13.0 Hz, 1H), 4.65 (s, 1H), 1.21 (s, 6H).

stabilized

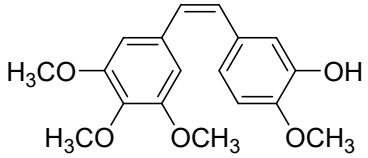


(*Z*)-2o

Colorless solid. Yield 90%. known compound [6].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 3H), 7.75 – 7.74 (m, 1H), 7.64 (dd, J = 8.5, 1.8 Hz, 1H), 7.45 (pd, J = 6.9, 1.5 Hz, 2H), 6.88 (dd, J = 17.6, 10.8 Hz, 1H), 5.87 (dd, J = 17.6, 0.7 Hz, 1H), 5.34 (dd, J = 10.8, 0.7 Hz, 1H).

Combretastatin A-4



Yellow solid. Yield 87%. known compound [7].

1H NMR (600 MHz, $CDCl_3$) δ 6.92 (d, J = 2.0 Hz, 1H), 6.80 (dd, J = 8.2, 2.0 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 6.53 (s, 2H), 6.47 (d, J = 12.2 Hz, 1H), 6.41 (d, J = 12.2 Hz, 1H), 5.50 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.70 (s, 6H).

References

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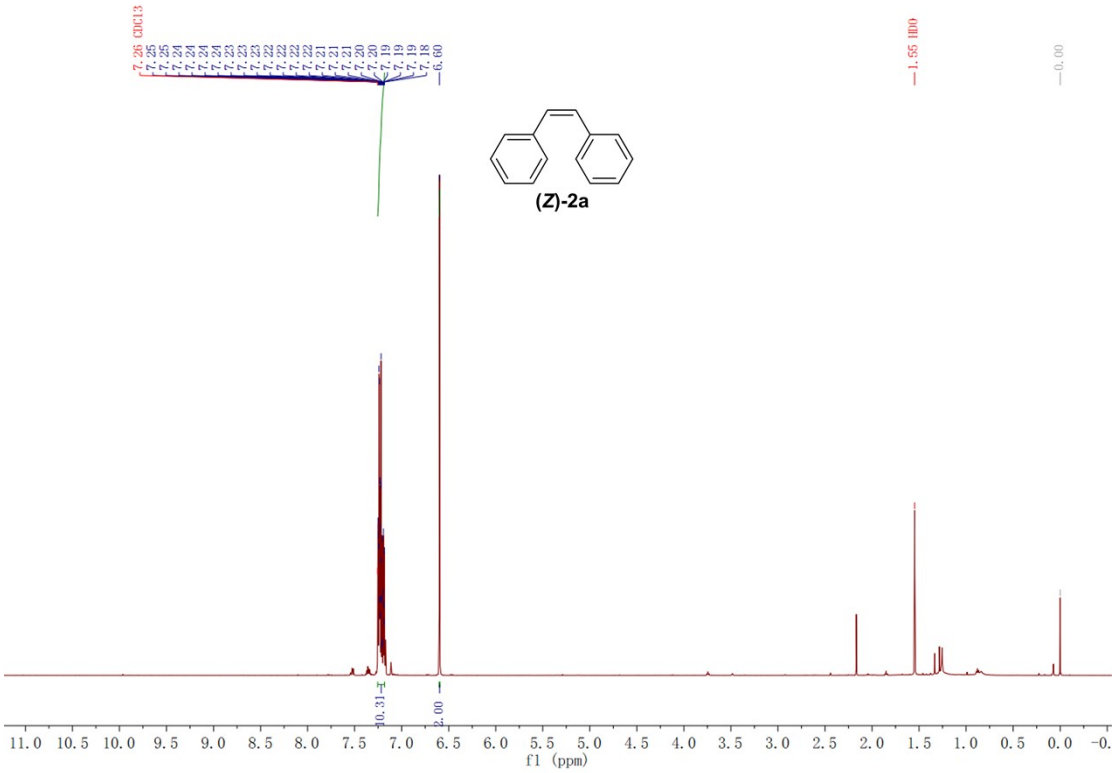
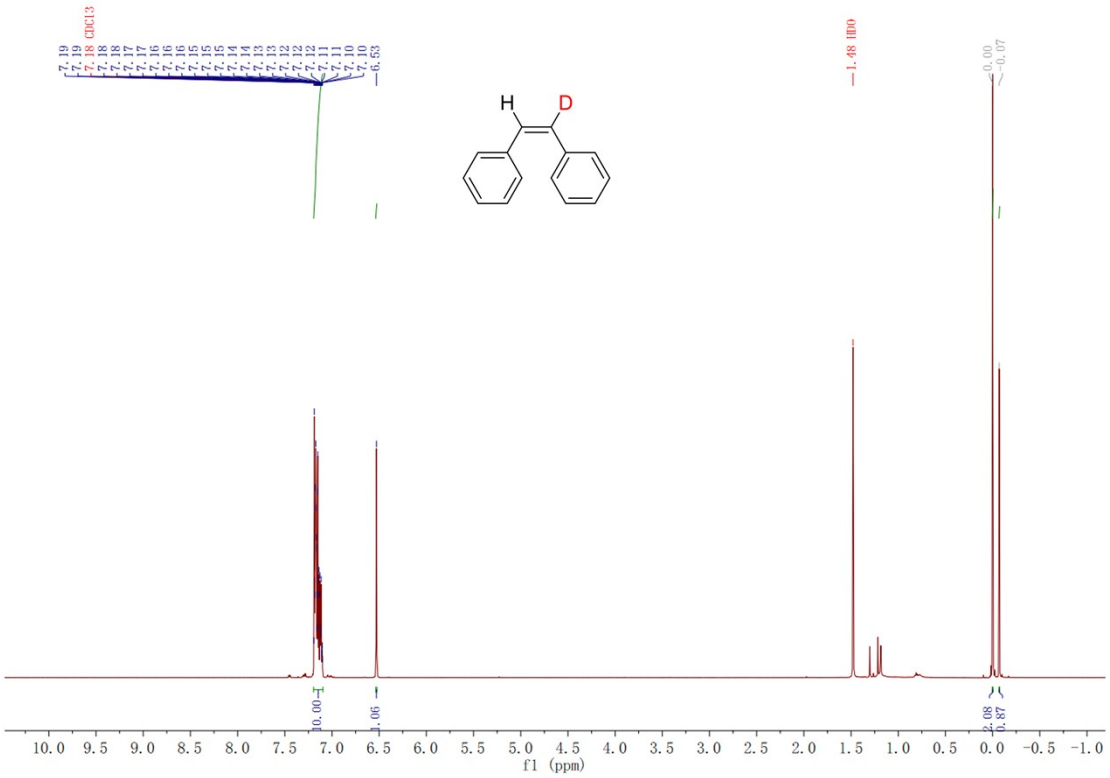
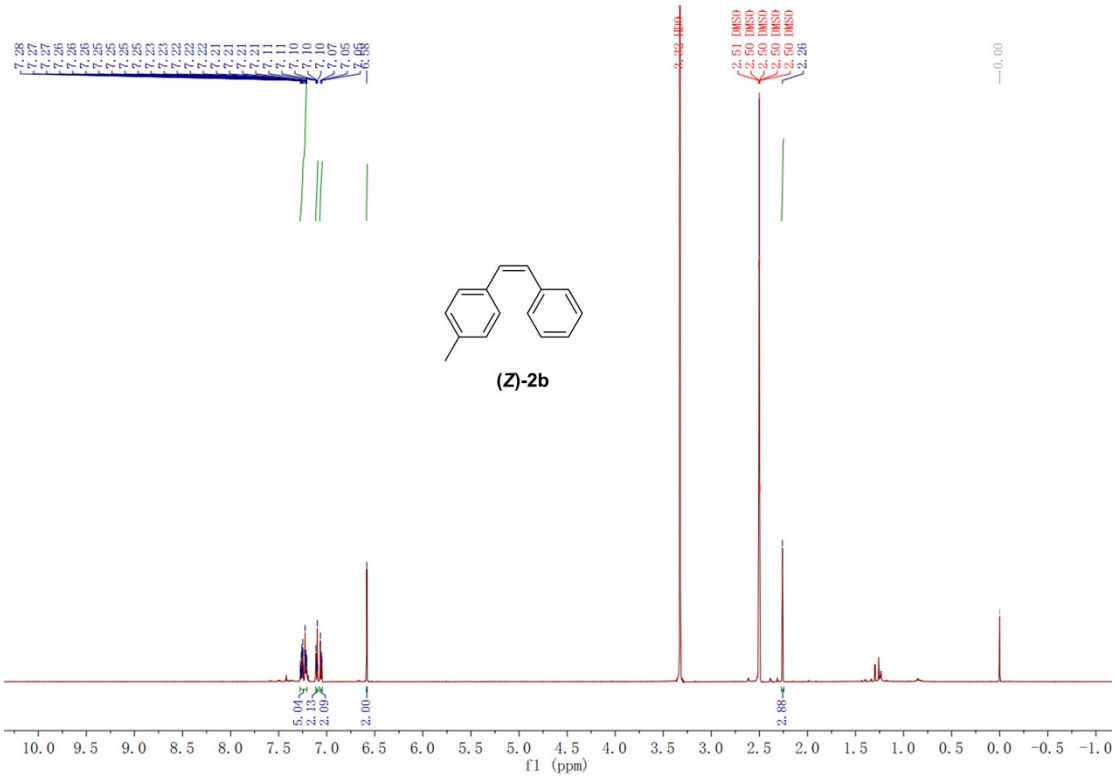
NMR Spectra



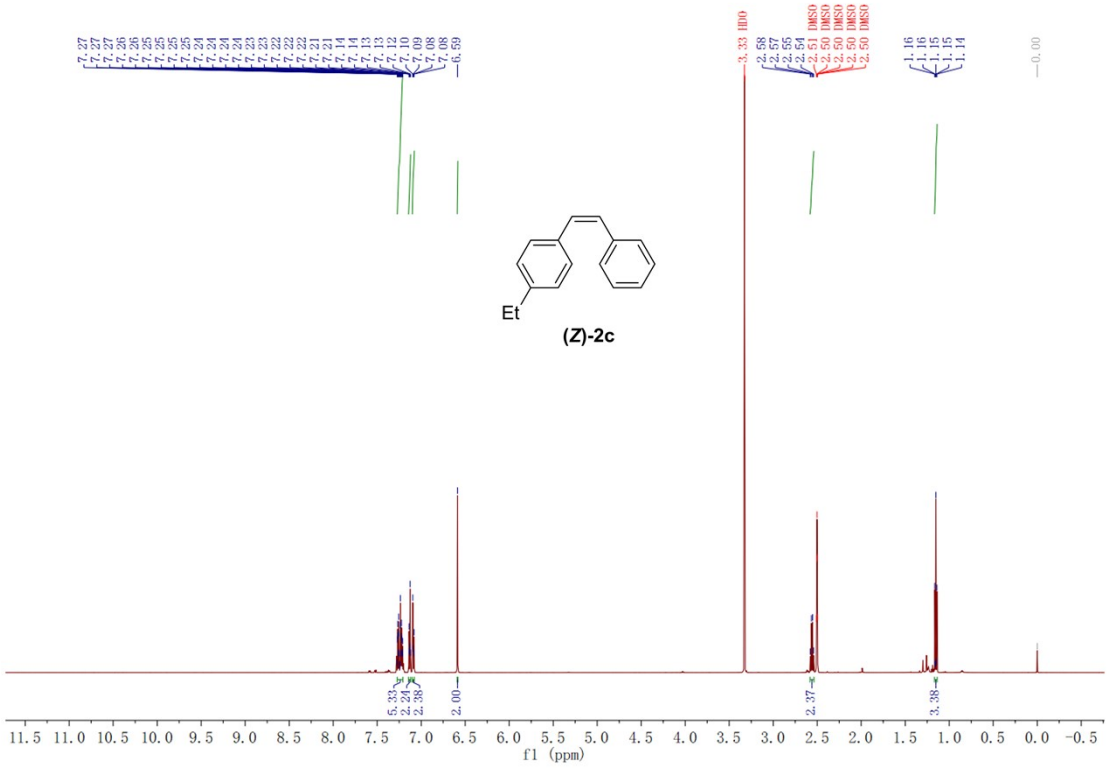
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (*Z*)-2a



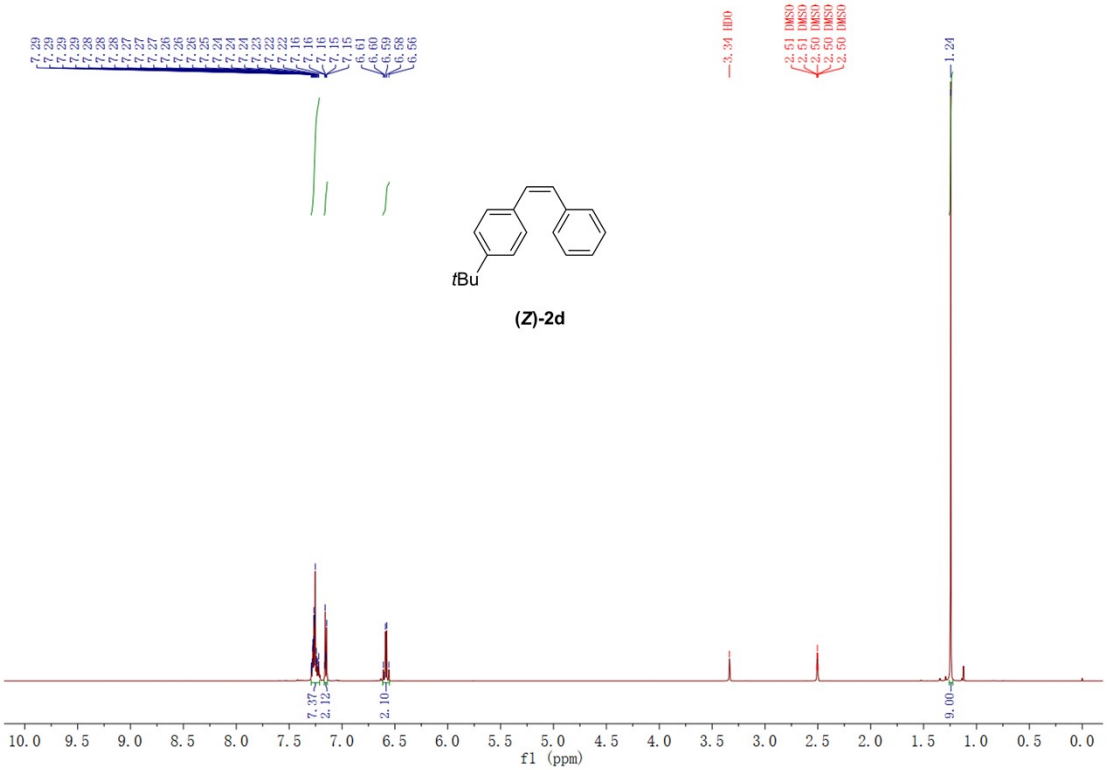
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of mono-deuterium (*Z*)-2a



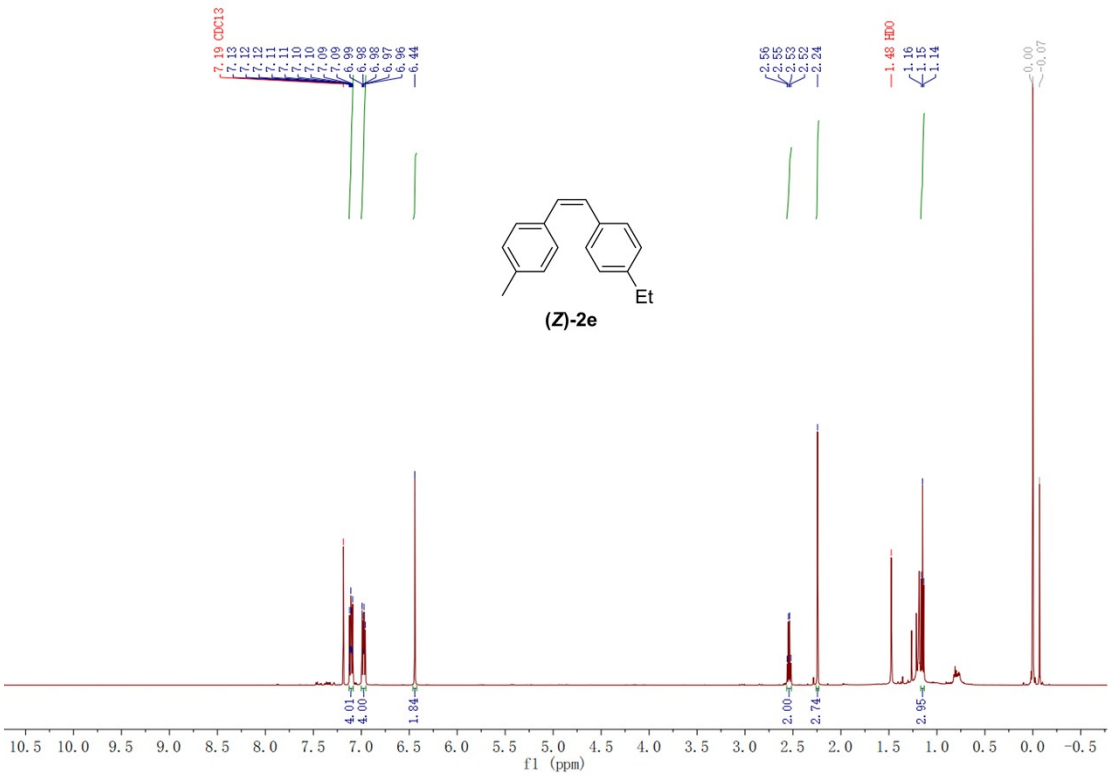
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*Z*)-2b



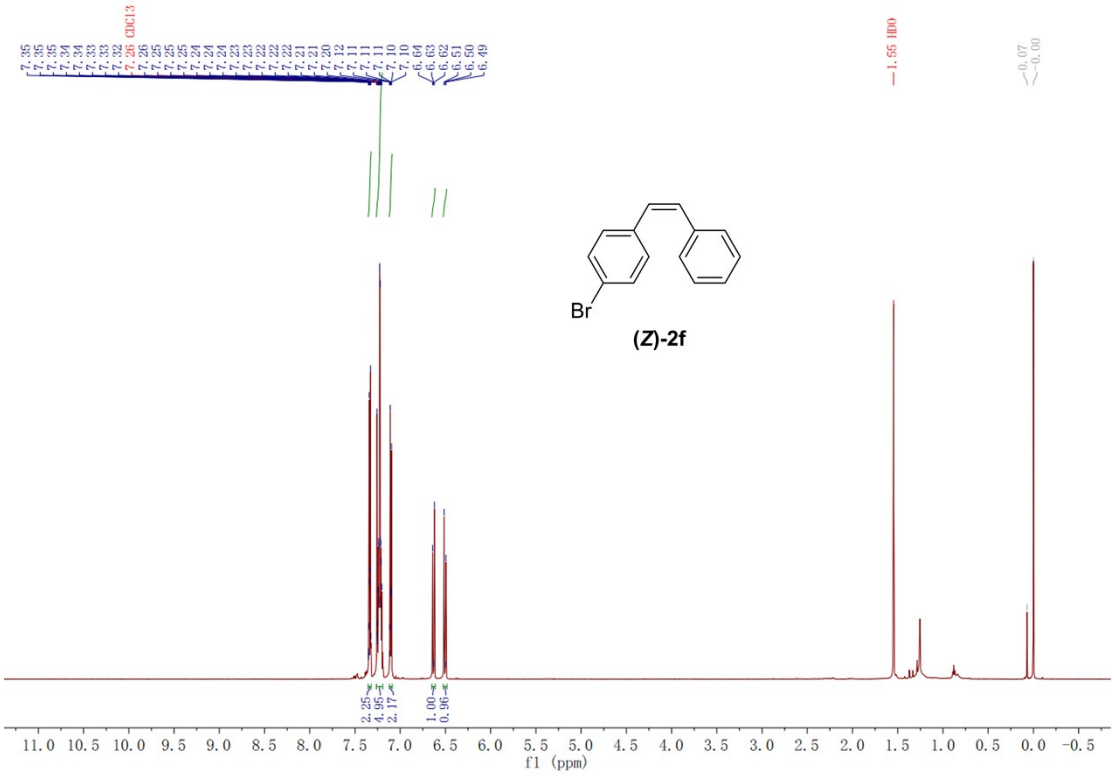
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*Z*)-2c



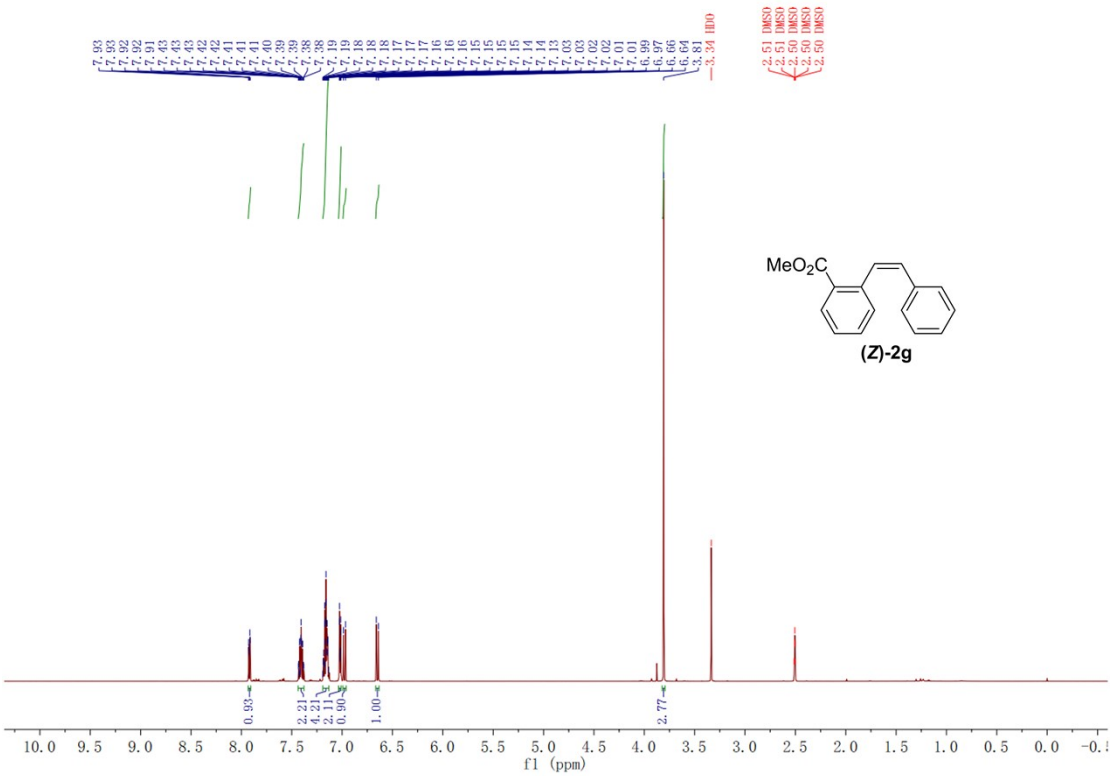
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*Z*)-2d



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (*Z*)-2e



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (*Z*)-2f



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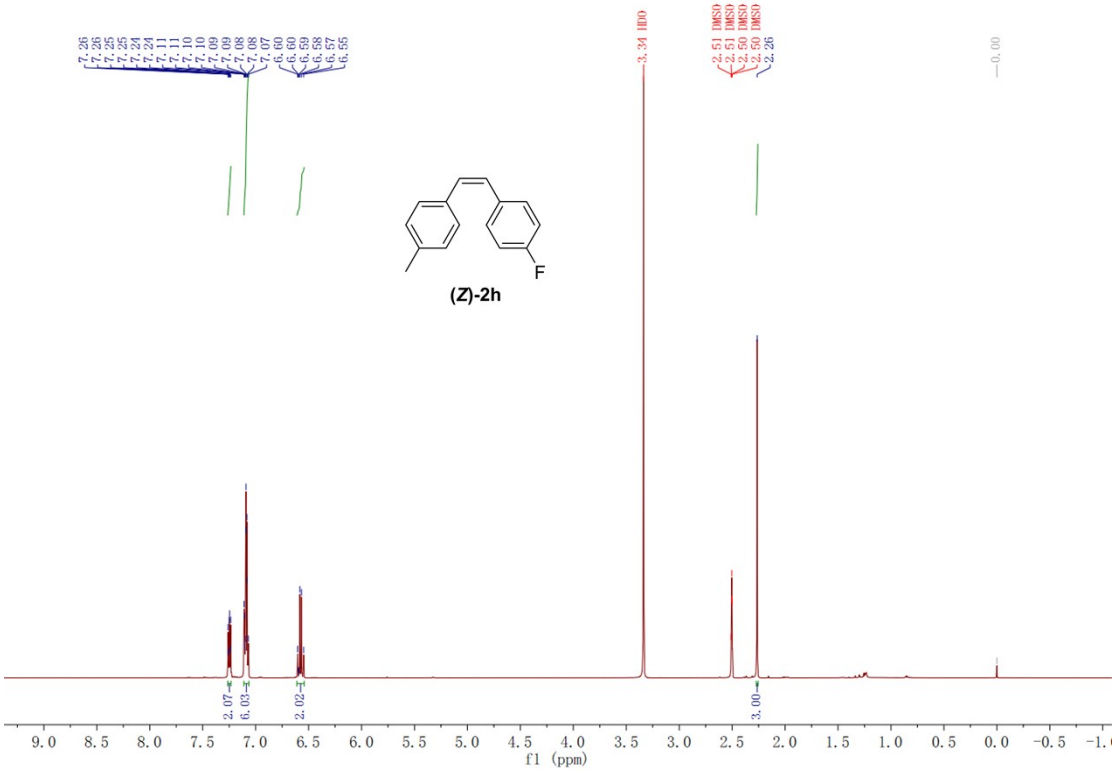
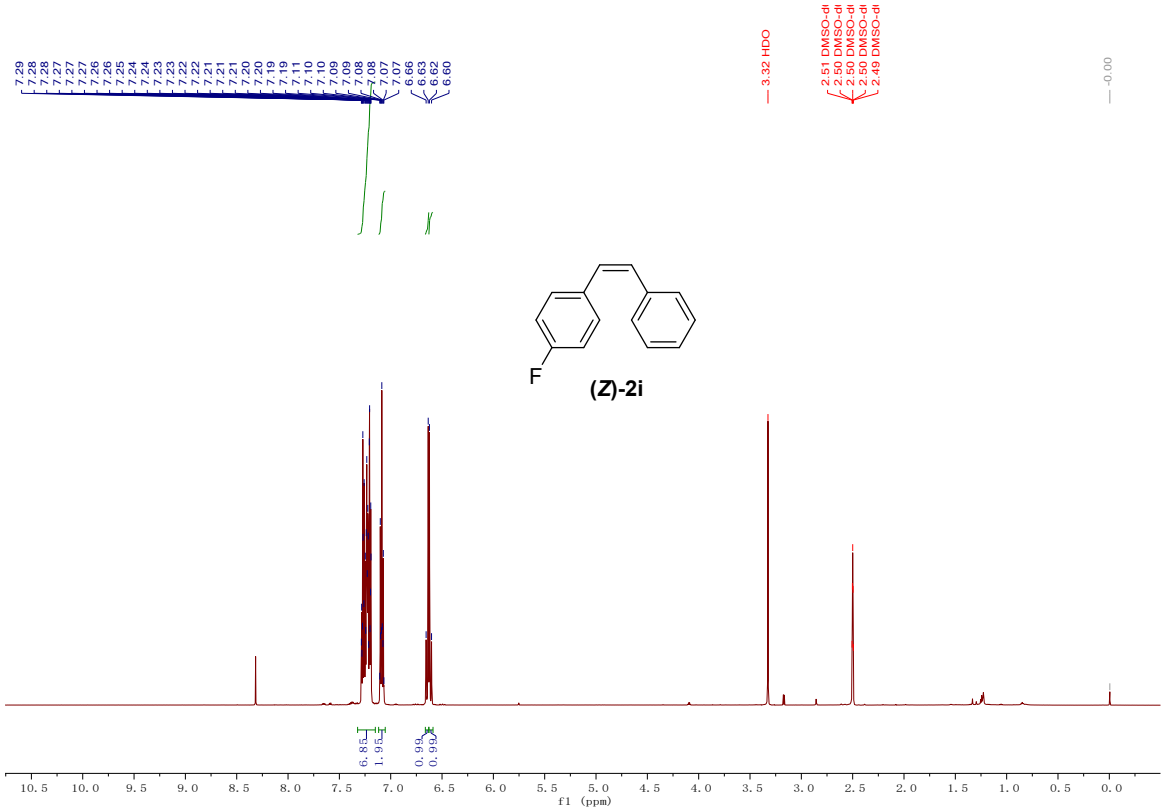
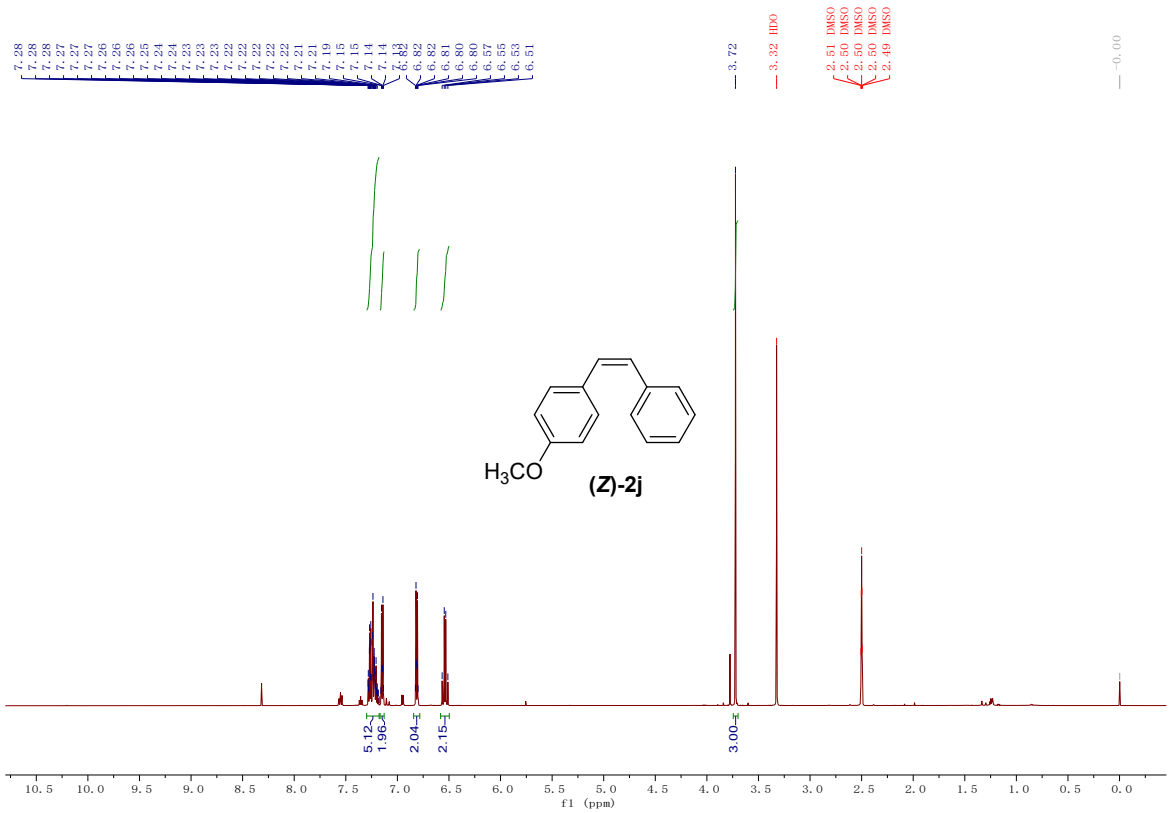


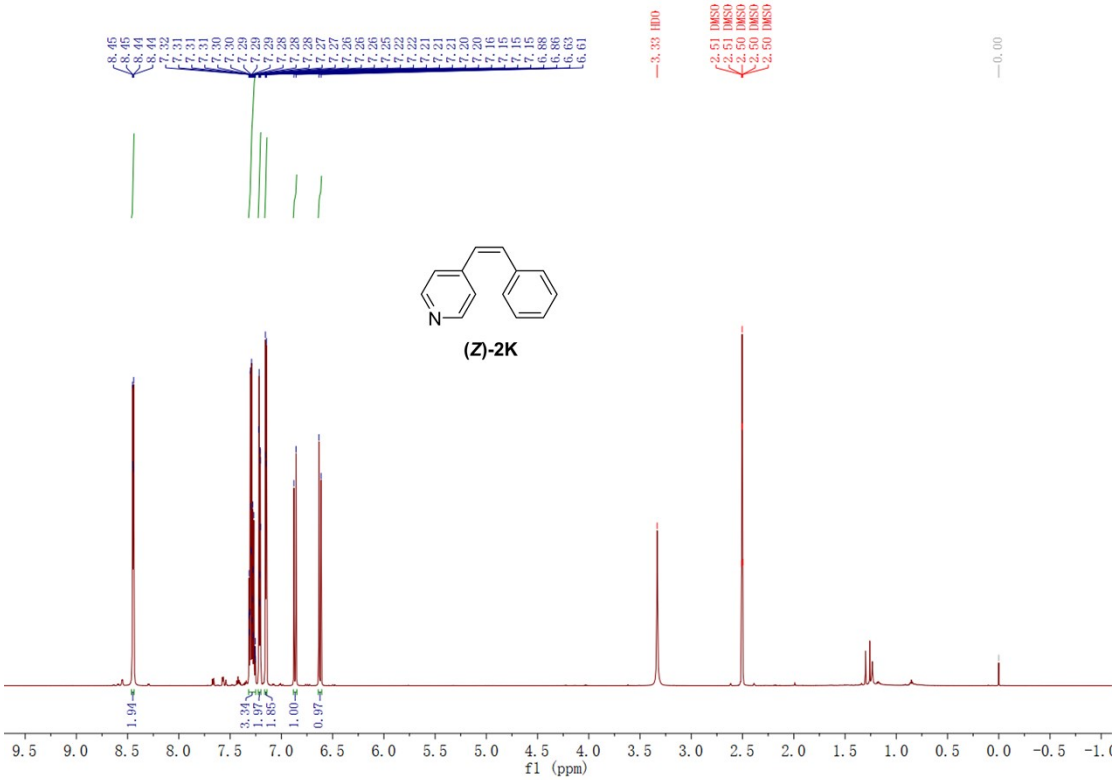
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*Z*)-2h



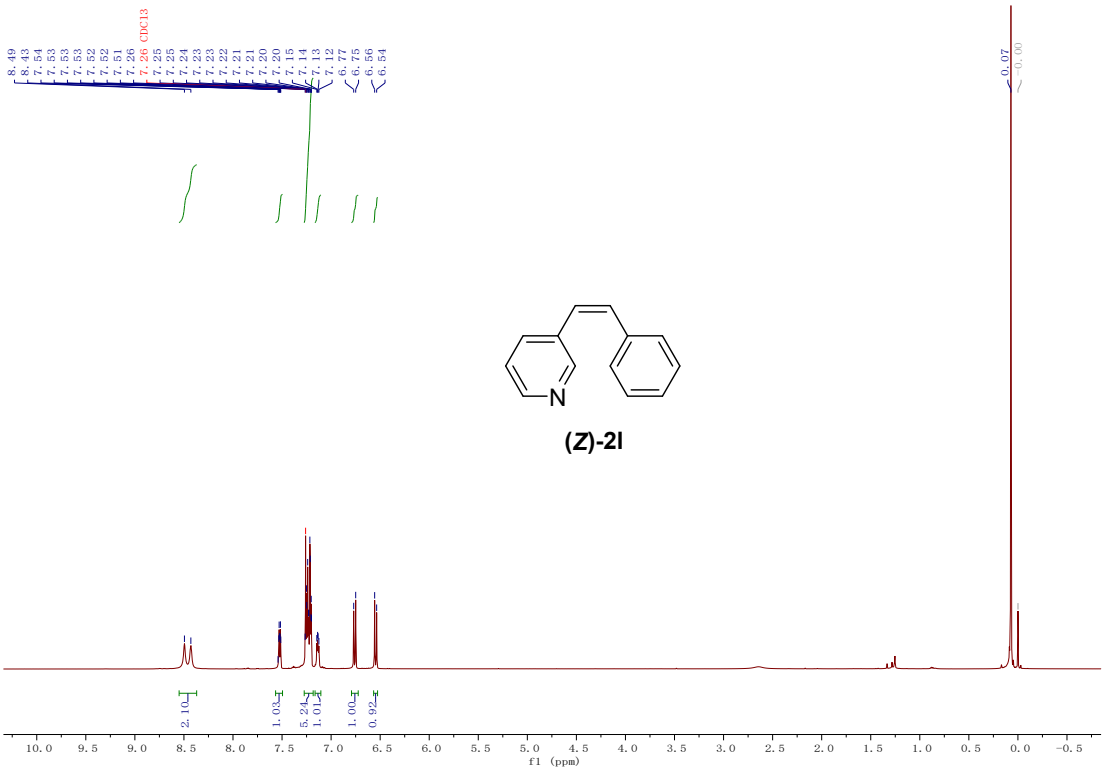
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*Z*)-2i



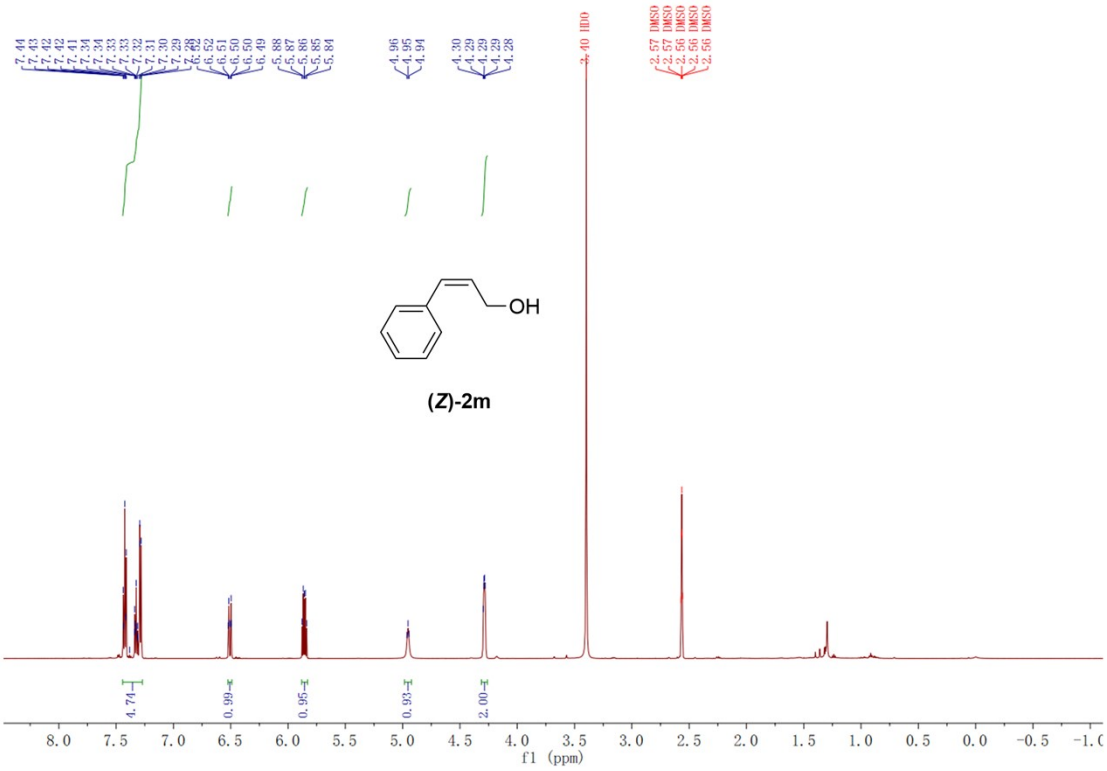
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*Z*)-2j



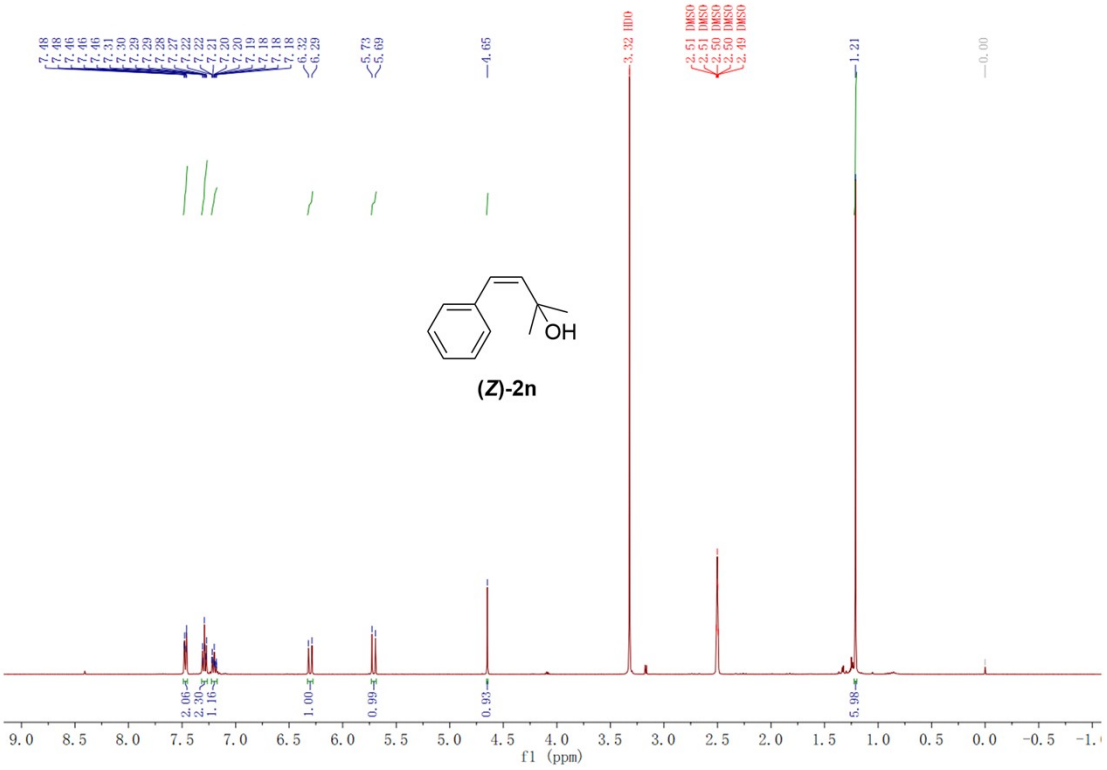
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*Z*)-2k



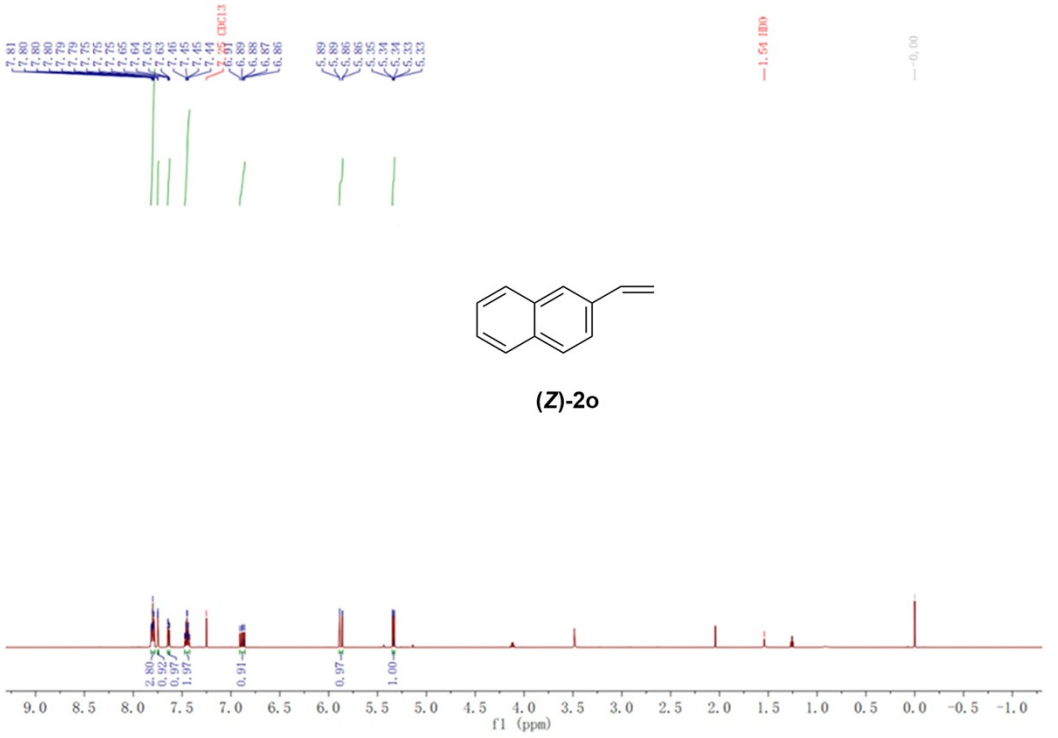
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (*Z*)-2l



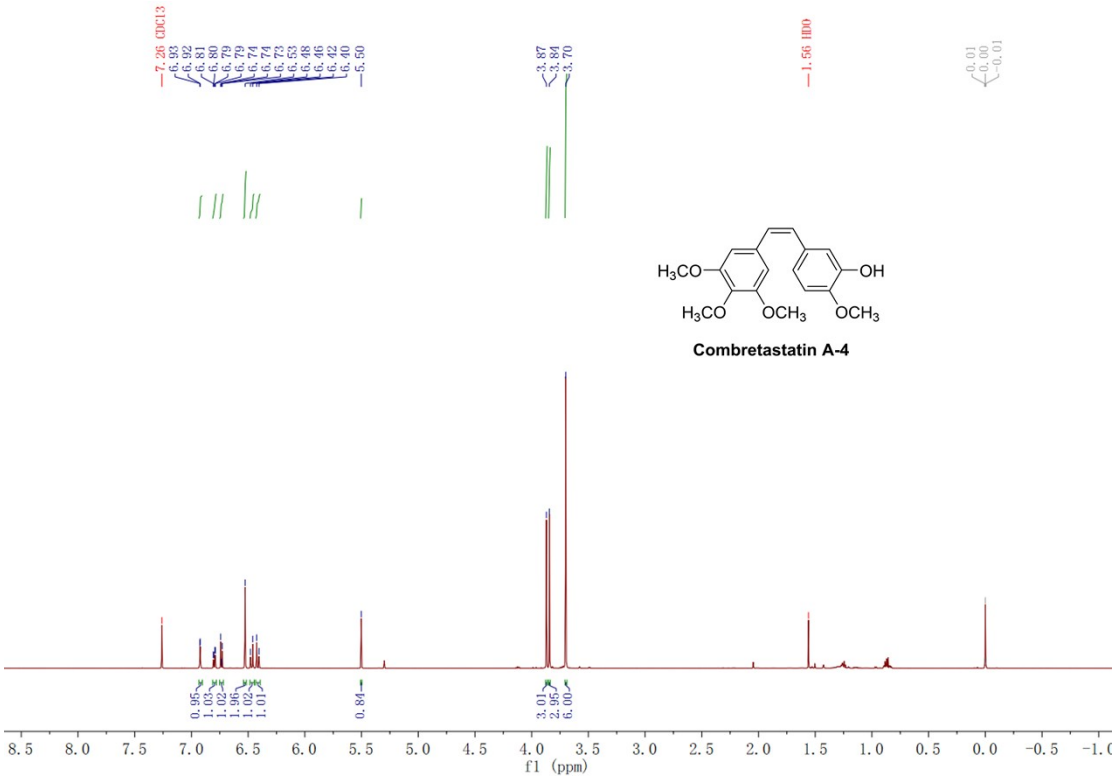
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*Z*)-2m



^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*Z*)-2n



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (*Z*)-2o



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of Combretastatin A-4